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GB 1446856 GB 1384873

(58) Field of search
C1J
F4B

(54) Ceramic structure

(57) A ceramic structure comprises a reticulated ceramic portion defined by a plurality of interconnecting webs and a ceramic sheet or coating portion sintered to the webs along a surface defined by one side of the sheet or coating. The ratio of the thickness of the sheet or coating to the average thickness of the interconnecting webs is less than ten.

The fired ceramic structure may be used as a molten metal filter, heat exchanger, kiln furniture, furnace lining, catalyst support, or filter for pollutants.

Fig. 1 illustrates a molten metal filter, Fig. 2 a portion of a ceramic heat exchanger and Fig. 4 a view of a furnace lining.

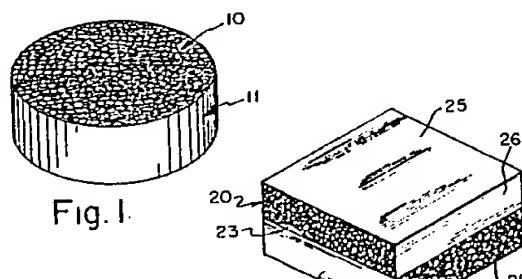


Fig. 1

Fig. 2

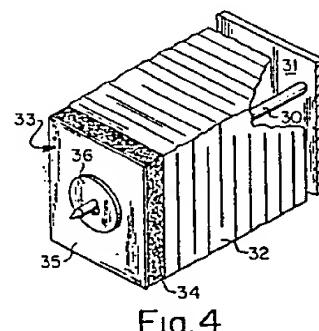


Fig. 4

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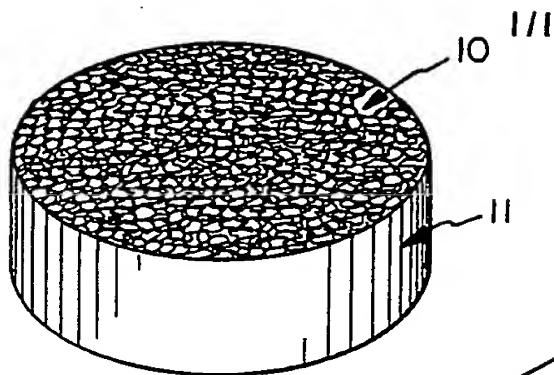


Fig. 1

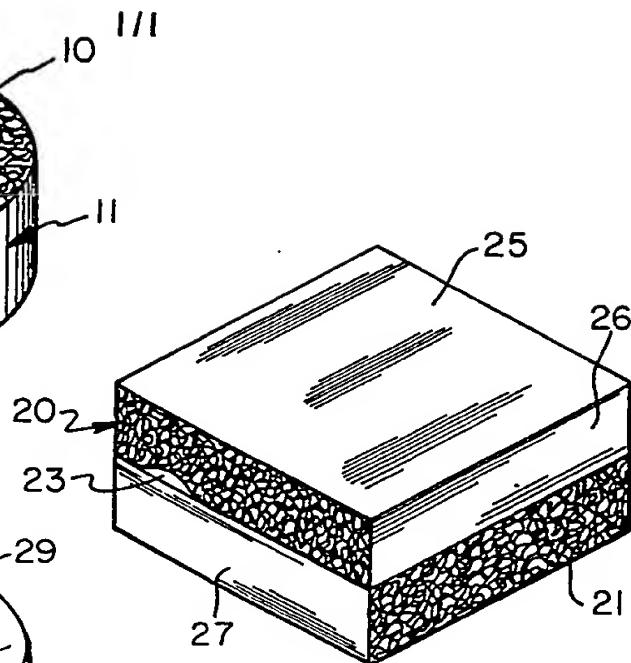


Fig. 2

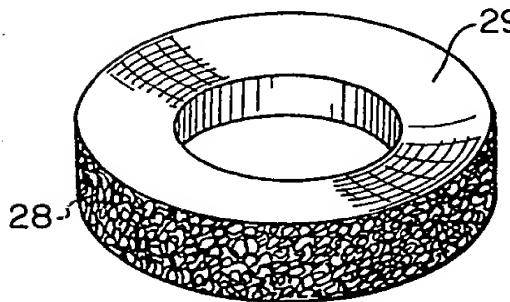


Fig. 3

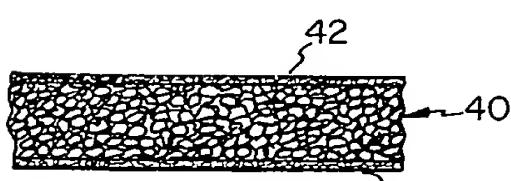


Fig. 5

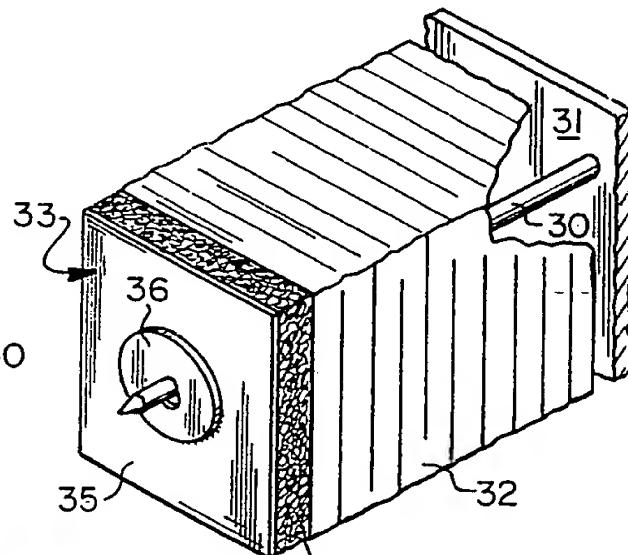


Fig. 4

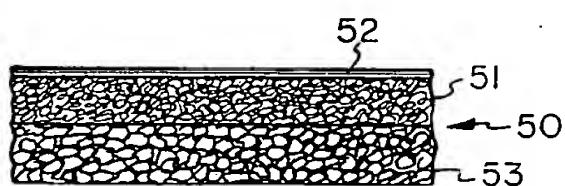


Fig. 6

SPECIFICATION**Ceramic structure and method of making same****5 Background of the invention**

Reticulated ceramics, in other words, sintered ceramic foams have found numerous applications. They comprise a unique two-phase system. A continuous solid phase is interspersed in a continuous pore phase extending in all directions. The solid phase is made from a relatively inert ceramic material (high temperature resistant, inorganic materials, usually oxides, carbides, etc.). They are useful for filtering hot fluids such as diesel exhaust gases and liquid metals and as a catalyst support frame. Methods of producing a reticulated ceramic are disclosed in Schwartzwalder et al. U.S. Patent No. 3,090,094 and British Specification No. 916, 784.

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Extremely thin ceramic sheets, say less than one mil (10^{-3} inch or about .04 millimeter) thick have been used for sometime to manufacture substrates for thick film technology, multi-layer capacitors, and so forth.

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15 A process for forming thin ceramics is described in Park U.S. Patent No. 2,966,719 and in an article entitled "Forming Thin Ceramics" by James J. Thompson, *Ceramic Bulletin*, Vol. 42, No. 9, (1963) pages 480-481.

15

It is an object of this invention to provide reticulated ceramics having an integral, thin surface or coating as a partition to close off the pore phase at selected locations and yet to retain the desirable properties of the reticulated ceramic. It is a special object of this invention to provide a ceramic article having a reticulated portion and a thin ceramic coating or sheet portion sintered together and matched to minimize thermal shock.

20

In the prior art, the surfaces of reticulated ceramics have been dipped in a slurry of finely divided ceramic to fill a sufficient number of pores in communication with the surface to seal the surface. The thickness of the continuous layer formed in this way is unpredictable and tends to be many times the thickness of the webs comprising the reticulated portion. The coarser the pores of the reticulated portion (say less than thirty pores per inch) the more difficult to provide a thin continuous layer by the dipping process. Nevertheless, as may be expected, the surface layers formed by the dipping process are well knit to the reticulated layer being in contact with internal web surfaces. Applicant has found that an article with improved properties can be formed by a technique that results in much less contact between the web surfaces and the surface layer.

25

25 Moreover, the surface layer will have an easily controlled uniform thickness. The articles made according to this invention will have improved thermal shock resistance due to the matching of the average thickness of the webs with the thickness of the surface layer and the more than adequate joining between the surface layer and the reticulated portion.

30

30 It is often desirable for refractory materials to be inert to elevated temperatures, corrosive environments and rapid changes in temperature while maintaining their strength and structural integrity. It is also desirable to maximize these properties while minimizing heat capacity and thermal conductivity. There are many types of refractories available today ranging from the very dense fused cast types to the highly insulating fiber types. The fiber refractories have very low thermal conductivity and heat capacity which is desirable. The shortcomings of fiber refractories are low load bearing capability and low corrosion

35

35 resistance along with shrinkage at the upper use temperature limits. The dense and insulating type refractories generally have good strength at temperature and are capable of being formed from corrosion and erosion resistant materials. The shortcomings of these materials, be it the preformed or monolith type, and are that they have relatively high heat capacity due to their inherent mass. Due to the high heat capacity, the energy requirements to bring these materials to temperature is much greater than the fiber refractories.

40

40 It is an object of this invention to provide an improved refractory material, either alone or in conjunction with fiber refractories which will not compromise the desired load bearing properties and corrosion-erosion resistance for low heat capacity. This ceramic refractory structure or reticulated ceramic possesses good load bearing strength and corrosion-erosion resistance along with low thermal conductivity, low heat capacity and excellent thermal shock resistance.

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50 Summary of the invention

Briefly, according to this invention, there is provided a ceramic structure comprising a reticulated ceramic portion defined by a plurality of interconnecting webs and a ceramic surface coating or ceramic sheet sintered to the webs along a surface defined by one side of the coating or sheet. The ratio of the average thickness of the coating or sheet to the webs forming the reticulated ceramic is less than ten.

50

55 In the sheet embodiment, the sheet portion has a thickness less than the average thickness of the interconnecting webs. Preferably, the average thickness of the interconnecting webs is less than about one millimeter. Still further, it is preferred that the thickness of the sheet portion be less than about 0.5 millimeter.

55

60 In the coating embodiment, the coating has substantially the same composition as the reticulated ceramic portion. The reticulated ceramic portion has a pore distribution between 5 and 125 pores per linear inch (ppi) and the coating has a thickness less than 3 millimeters. Preferably, the coating is at least 0.25 millimeter thick. The ratio of the average thickness of the coating to the average thickness of the webs forming the reticulated ceramic portion is between 1 and 10.

60

65 There is also provided a method of manufacturing a ceramic structure comprising the steps for preparing a

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reticulated ceramic portion and separately preparing a leather-hard ceramic sheet. The ceramic sheet is applied to the reticulated ceramic portion by first applying a ceramic slurry to the reticulated ceramic portion but without filling the pores at the surface thereof. The leather-hard ceramic sheet is brought into firm contact with the reticulated ceramic portion where the slurry has been applied. Thereafter, the composite 5 structure is fired to form a sintered ceramic bond between the reticulated ceramic portion and the ceramic sheet.

There is also provided a method of manufacturing a ceramic structure comprising the steps of preparing a reticulated ceramic portion and subsequently providing a coating thereon. The coating is provided by troweling, brushing or spraying a suitable ceramic slurry gently over at least a portion of a surface of the 10 reticulated ceramic portion. The sprayed coatings have a thickness between about 0.25 and 0.50 millimeter and are suitable for use on reticulated ceramic portions having a pore size between about 65 and 125 ppi. 15 The coatings provided by troweling or by the use of a doctor blade have a thickness between about 0.5 and 3 millimeters and are suitable for use with reticulated ceramic portions having a pore size from as large as 5 ppi to very fine. The larger the pore size the larger the thickness of the coating tends to be. The coated structure is fired to form a sintered ceramic bond between the reticulated ceramic portion and the coating.

The ceramic structure defined herein may comprise a filter for molten metal in which case the reticulated ceramic portion has a surface wrapped with the ceramic sheet or provided with a ceramic coating which surface is substantially parallel to the direction of flow through the filter. The structure according to this invention may comprise a heat exchanger in which case it comprises two reticulated ceramic portions 20 separated by a thin ceramic sheet sintered to each of the reticulated ceramic portions. Means are provided to direct flow of hot fluids through the reticulated ceramic portion on one side of the ceramic sheet and means are provided to direct flow of cooling fluid through the reticulated ceramic portion on the other side of the ceramic sheet. The ceramic structure defined herein may be used as kiln furniture comprising a reticulated ceramic base having a thin ceramic surface. Depending upon the application, the coating may be placed 25 adjacent to or away from the ware being supported by the kiln furniture.

Still further, the ceramic structure disclosed herein may be used by itself or in conjunction with fiberboard or fiber blanket as a refractory material for lining furnaces.

The drawings

30 Further features and other objects and advantages of this invention will become clear from the following detailed description made with reference to the drawings in which
 Figure 1 is a pictorial view of a ceramic filter for molten metal according to this invention;
 Figure 2 is a pictorial view of a portion of a ceramic heat exchanger according to this invention;
 Figure 3 is a pictorial view of an item of kiln furniture according to this invention;
 35 Figure 4 is a pictorial cut away view of a furnace lining according to this invention;
 Figure 5 is a section through a special ceramic structure; and
 Figure 6 is a section through another special ceramic structure.

Description of the preferred embodiments

40 Figure 1 illustrates a useful article according to this invention which is a ceramic filter for molten metal. A central portion 10 comprises reticulated ceramic having the outward shape of a disk. The outer cylindrical surface of the disk has a thin ceramic coating or sheet 11 sintered thereto. The cylindrical surface is, of course, generally parallel to the flow of hot metal through the pores of the reticulated ceramic. The coating or the wrapping of the reticulated ceramic with a ceramic material that becomes integral therewith increases 45 the strength of the entire unit. Figure 1 actually illustrates an insert to be rested in a supporting structure comprising a funnel or the like for directing the molten metal to the reticulated ceramic filter. The coated or wrapped molten metal filter is less friable during handling and insertion into a pour cup or tundish. It also prevents the metal from short circuiting the filter by flowing to the peripheral edge of the filter and out along the filter funnel interface. It also improves the compressive strength of the insert.

50 Ceramic materials suitable for making filters for vacuum induction melted super alloys are mullite, partially stabilized zirconia, and alumina (90-98%). Mullite and zirconia are preferably used due to their better thermal shock resistance. The pore sizes most commonly used are 10, 20, and 30 ppi with 10 and 20 ppi being the preferred. The 30 ppi will generally have the highest filtration efficiency but the reduced flow through the filter can make this pore size prohibitive for many applications.

55 For making filters for air-melted ferrous alloys a strong, thermal shock, and creep resistant material is required. The materials for these applications are preferably partially stabilized zirconia, various grades of high alumina and mullite for smaller volume pores. Pore sizes of 5-7 ppi, 10 ppi and 20 ppi are used for this application.

For air-melted nonferrous metals, mullite is preferred along with the alumina compositions. Pore sizes 60 ranging from 10 ppi to 65 ppi have been used successfully. The promising results in one application involved using a 65 ppi mullite filter in a cylindrical geometry. The fine pore filters (30 ppi, 45 ppi, 65 ppi) show the highest filtration efficiency.

Figure 2 illustrates a useful article according to this invention; namely, a ceramic heat exchanger. It is comprised of a first reticulated ceramic portion 20 and a second reticulated ceramic portion 21. Between the 65 two reticulated ceramic sections or portions is a thin sheet of ceramic 23, (shown in Figure 2 because a

portion of the reticulated ceramic portion is broken away for illustration purposes). The exterior walls of the two reticulated ceramic portions are wrapped with ceramic sheet 25, 26, and 27. The arrangement is such that heat exchange fluids can flow perpendicular to each other on opposite sides of the sheet 23. Both reticulated ceramic portions have webs that are sintered directly to the sheet. In other words, the thin 5 separating sheet is integral with the two adjacent reticulated ceramic portions. Hence, heat is transferred from one heat exchange fluid to the webs of one reticulated ceramic portion, then through the sheet, and then to the webs of the other reticulated ceramic portion and finally to the second heat exchange fluid. It is not essential that the flow of the heat transfer fluids be perpendicular. The exterior walls of thin sheet 10 ceramic can be arranged for countercurrent flow or any flow pattern desired. The heat exchanger may comprise many more than the two reticulated ceramic portions shown in Figure 2, with alternate layers 15 arranged to carry alternate warmer and cooler heat transfer fluids.

Figure 2 illustrates an insert for a heat exchanger which could be arranged in a structure defining plenum chambers on all four sides sealed from each other for the introduction and removal of the heat transfer fluids to and from the pores of the reticulated ceramic sections. In a fixed heat exchanger it is necessary to separate 15 the dirty hot gas (exhaust gas) from the incoming air which one desires to preheat (combustion air). Ideally, one would like to transfer all the heat from the exhaust gas to the combustion air without allowing the gases to physically mix. Therefore, the thinnest possible separation of the gases is the most desirable. This can be accomplished very efficiently by the alternate stacking of reticulated ceramic sections with the impervious separating layer formed by the thin ceramic sheet. The ability to physically separate the two gases with a 20 very thin wall improves heat transfer, thus the efficiency of the heat exchanger. The thin, separating sheet reduces the thermal gradient and therefore the thermal stress created by the thermal gradient. Another reason for the improved efficiency of heat exchangers using reticulated ceramic materials in conjunction with the thin ceramic sheet integral therewith is the improved heat transfer from the gas to the thin sheet via the webs. The webs act as conduction fins transferring heat from the hot gas to the separating sheet and 25 back to the webs in the cool gas stream. The tortuous path of the gas through the reticulated ceramic portion generates turbulent flow which removes the static gas layers at the web or wall gas interface. This further improves heat transfer. The reticulated ceramic material improves heat transfer by all three modes; namely, conduction, convection, and radiation.

Figure 3 illustrates a useful article according to this invention comprising an item of kiln furniture for a 30 plate. The item comprises a base portion 28 of reticulated ceramic, the upper side of which is shaped to conform to the underside of the plate or ware to be fired. Allowance for shrinkage of the ware is made. The shaped surface is covered with a thin layer of ceramic integral with the underlying reticulated ceramic base. It is often desirous to have a smooth, flat surface on which to set the ware to facilitate the ability of the 35 shrinkage ware to slide easily. This is accomplished by applying a coating or a thin ceramic sheet 29 to the surface of the reticulated ceramic base. There exists a minimal increase in heat capacity of the base which is advantageous because it permits the available heat to be used to process the ware.

There is a continuous effort to reduce the mass of the kiln setting material to enhance fuel savings. To 40 reduce firing cycle times, kiln furniture must be more thermal shock resistant. The use of reticulated ceramics has a tremendous potential especially in the electronics field where the ratio of setter mass to product mass is large. Low mass furniture will be best suited for situations where a high setter to product mass ratio exists since these materials may potentially creep under high loads at upper use temperatures. Mullite and high alumina products of the finer pore sizes are the preferred materials. It should be noted that 45 in applications such as setter plates for the electronic industry, where the ceramic components contain a high percentage of organics, the porous nature of the reticulated ceramic is advantageous because there is less pressure developed at the contact surfaces when the volatiles are burning off. In this case, the coating on the reticulated ceramic portion is not placed adjacent the workpiece.

Referring now to Figure 4, there is shown a portion of a furnace liner according to this invention. A ceramic anchor 30 is secured to a metal furnace shell 31. Inwardly of the shell is a refractory fiber blanket 32. Inwardly of the fiber blanket is a composite ceramic structure 33 substantially as described herein. The composite 50 ceramic comprises a reticulated ceramic portion 34 and a thin ceramic sheet 35. It is preferred that the composite refractory be comprised of at least one reticulated ceramic portion between two thin sheet portions. Moreover, it is preferred that the composite refractory be comprised of two or more reticulated ceramic portions separated by a plurality of substantially parallel thin sheet portions. The composite refractory should be oriented such that the thin sheet portions are substantially perpendicular to the 55 direction of heat flow. The anchor passes through an opening in the composite ceramic structure 33 which is secured to the anchor by key 36. The composite ceramic structure and refractory fiber blanket can be formed into modular units with the refractory fiber blanket being bonded to the reticulated ceramic side of the composite structure with a refractory cement. A suitable refractory cement might be calcium aluminate cement. The refractory fiber blanket may be replaced by another ceramic fiber refractory felt, a refractory 60 fiber block or refractory fiberboard. Ceramic fiber refractories are all slightly compressible when new.

The module, a portion of which is shown in Figure 4, can be easily installed in a furnace and provides the excellent thermal insulation of fiber refractories and an erosion resistant surface which will not shrink (say at 3,000°F in the case of an alumina refractory sheet). It is more durable than mere fiber refractory and does not have the problem of dusting and damage when brushed against. The dusting and damage problems are very 65 apparent with fiber insulation after a short term use at high temperatures. At these temperatures

embrittlement occurs due to sintering and recrystallization. The unprotected ceramic fiber refractory loses its compressibility.

The need for a low mass, highly insulating material that is rigid, non-friable, corrosive/erosive resistant and does not shrink at upper use temperatures commends reticulated ceramics as a furnace lining material.

- 5 Using the reticulated ceramics in conjunction with fiber insulation enhances the fiber lined furnace concept. 5
- These panels are preferably made from mullite with pore sizes ranging from 45 ppi to 100 ppi. The surfaces are closed off by applying a dense coating to the reticulated ceramics. With this system, the desired properties such as thermal shock resistance, low thermal conductivity, minimal heat storage along with ease of application are still intact while the common fiber problems such as friability, dusting, erosion or 10 corrosion and shrinkage due to devitrification and sintering are greatly improved. Another important consideration is that these panels are load bearing therefore burner blocks can be supported by the hot face material. This is very important when retrofitting a brick furnace with fiber insulation. These materials can be made out of high performance oxides such as 98% alumina and zirconia which is a difficult and expensive process when forming fibers from the same materials.
- 15 According to yet another embodiment of my invention, there is provided a composite ceramic structure in which the reticulated ceramic is comprised of more than one layer of reticulated ceramic with each layer having a different pore size. The ceramic structure might, for example, have a very fine pore structure near the surface and a coarser pore structure in the interior. 15

Referring to Figure 5, there is shown a portion of a composite ceramic structure 40 having a reticulated 20 interior portion of a pore size ranging from 7 to 45 ppi and reticulated face portions 42 having a pore size ranging from 30 to 100 ppi. The thin fine face portions 42 are maintained leather-hard prior to affixing to the interior portion and are applied thereto following spraying the surface of the large pore reticulated ceramic (which may be leather-hard or drier) with a suitable ceramic slurry. 20

Referring now to Figure 6, there is illustrated yet another embodiment of this invention comprising a 25 composite ceramic structure 50 having a small pore reticulated ceramic portion 51 sandwiched between a thin ceramic sheet 52, and a coarser pore reticulated ceramic portion 53. The pore size of the coarse pore portion 53 is from 7 to 45 ppi and of the small pore portions 51 is from 32 to 100 ppi. This structure is especially suited for kiln shelves with a thin ceramic sheet selected appropriate to the ware being supported thereby. In the electronics field, components are very sensitive to the stoichiometry. The composition of the 30 components can change by interaction between the components and the supporting surface during firing. For example, bismuth titanate could be fired upon a composite structure according to this invention as shown in figure 6 by making the thin ceramic sheet 52 of a material containing bismuth, to thus maintain the volatile bismuth content of the bismuth titanate components placed thereon for firing. 30

A structure as described with reference to the drawings may be fabricated as follows: The reticulated 35 ceramic portion is prepared by immersing an open celled, porous, organic material (for example, urethane foam) in a slurry of finely divided ceramic powder (for example, mullite) having a binder therein. In this way, the walls of the porous material are coated. Excess slurry is removed. The coated material is then fired to burn out the organic material and form a ceramic bond (sintered bond) between the finely divided ceramic particles. In this way, the internal structure of the porous material is replicated. In an alternate embodiment, 40 the slurry is provided with a high temperature binder, such as a phosphate, and the initial firing is only sufficiently high to burn out the organic material but not to form a true ceramic bond (sintered bond). 40

The thin ceramic sheet is prepared as follows: A slurry is prepared having the same or a compatible chemistry as that used in the fabrication of the foam. Powders containing silica, alumina, magnesia, lithia, zirconia, zircon, titania, and so forth are useful. They are added to a liquid and mixed at high shear rate. To 45 this powder surfactants and organic binders such a polyvinyl alcohol, Hydrodyne, a trademarked product, glycerin, sodium hexametaphosphate, and so forth are added and dispersed. This slurry, having a solid weight percent from 40 to 80, is deaired under vacuum. A sheet is cast using a doctor blade on a glass plate heated to temperatures of 25 - 80°C. A release agent such as 0.5 weight percent of lecithin dissolved in 1,1,1-trichloroethane is first applied to the glass plate to facilitate the removal of the thin ceramic sheet. The 50 ceramic sheet might also be prepared in a continuous process. 50

The ceramic sheet is removed from the plate when it still contains 2 to 12% moisture. It is cut to the desired size and stored in a humidified environment having a relative humidity of greater than 80%.

The ceramic sheet is applied to the reticulated surface by first spraying a thin coating of ceramic slurry which has the same or compatible chemistry as the sheet and the reticulated ceramic portion upon the 55 reticulated surface. The coating does not, however, seal off the pores. The surfaces of the thin sheet and the reticulated ceramic portion are then joined together and allowed to dry. The composite is then fired to form a strong sintered bond between the sheet and the webs of the reticulated ceramic portion. 55

The physical properties of certain reticulated ceramics after firing are set forth in the following tables.

TABLE I

5	Lithium Aluminosilicate		5
	Maximum use temperature:	1250°C	
	Thermal shock resistance:	Excellent	
	Thermal expansion coefficient:	0.38×10^{-6} in/in/°C	

10 *Pore Size Dependent Properties*

10	ppi:	10	20	30	10
	Transverse Strength (psi):	75	125	190	
15	Compressive Strength (psi):	80	100	150	15
	Unit Density (g/cm ³):		0.36	0.34	
	Unit Porosity (%):		82.0	83.0	

20 TABLE II

20	Mullite		20
	Maximum use temperature:	1650°C	
25	Thermal shock resistance:	Good	25
	Thermal expansion coefficient:	4.90×10^{-6} in/in/°C	
	Creep rate:	0.15% deformation/hr. 5 psi load at 1500°C 10 ppi	

30 *Pore Size Dependent Properties*

30	ppi:	10	20	30	30
	Transverse Strength (psi):	203	333	—	35
35	Compressive Strength (psi):	228	445	—	
	Pore Size (mm):	1.186	0.746	0.614	
40	Web Size (mm):	0.674	0.481	0.283	40
	Unit Density (g/cm ³):	0.455	0.474	0.448	
	Unit Porosity (%):	78.31	76.73	81.15	

45 TABLE III

45	Zirconia (partially stabilized)		45
	Maximum use temperature:	1800°C	
50	Thermal shock resistance:	Excellent	
	Thermal expansion coefficient:	7.80×10^{-6} in/in/°C	
	Creep rate:	0.25% deformation/hr. 35 psi load at 1500°C 10 ppi	50

55 *Pore Size Dependent Properties*

55	ppi:	10	20	30	55
	Transverse Strength (psi):	324	489	—	
60	Compressive Strength (psi):	365	286	—	60
	Pore Size (mm):	1.407	0.835	—	
	Web Size (mm):	0.456	0.352	—	
	Unit Density (g/cm ³):	0.939	1.178	—	
65	Unit Porosity (%):	80.67	77.19	—	65

TABLE IV

	98% Alumina			
5	Maximum use temperature:	1750°C		
	Thermal shock resistance:	Fair		5
	Thermal expansion coefficient:	8.85×10^{-6} in/in/°C		
10	<i>Pore Size Dependent Properties</i>			
	ppi:	10	20	30
	Transverse Strength (psi):	217	472	419
15	Compressive Strength (psi):	323	411	—
	Pore size (mm):	1.305	0.825	0.673
	Web Size (mm):	0.578	0.335	0.318
	Unit Density (g/cm ³):	0.446	0.493	0.685
20	Unit Porosity (%):	80.88	78.35	70.49

TABLE V

	90% Alumina			
25	Maximum use temperature:	1700°C		25
	Thermal shock resistance:	Good		
	Thermal expansion coefficient:	6.52×10^{-6} in/in/°C		
	Creep rate:	0.15% deformation/hr.		
30		35 psi load at 1500°C		
		10 ppi		30

	<i>Pore Size Dependent Properties</i>			
35	ppi:	10	20	30
	Transverse Strength (psi):	114	144	—
	Compressive Strength (psi):	174	165	—
40	Pore Size (mm):	1.516	0.810	0.625
	Web Size (mm):	0.606	0.331	0.304
	Unit Density (g/cm ³):	0.435	0.442	0.504
	Unit Porosity (%):	79.83	78.83	75.39

45 Surface coatings are applied by various methods such as trowelling, brushing, spraying or with a doctor blade directly on the green pieces. Spray coating may be used with reticulated ceramics having a pore size from 65 ppi to 100 ppi.

An example of the formulation for a 2000 gram batch of 98% alumina spray coating slurry is as follows:

50	Alumina	1,960 grams	
	Silica	100 grams	
	Organic binder	200 grams	
	Surfactant	5 milliliters	
55	H ₂ O	1,000 milliliters	55

The materials are mixed under high shear until creamy then viscosity adjustments may be made. The surfactant aids in forming a dispersion of the ceramic in the liquids.

60 The viscosity range will be between 250 and 1500 centipoise with a desired viscosity of 500 centipoise. The slurry is sprayed at a pressure of 70 psi starting at a working distance of 2 inches making numerous passes and backing off to 4 inches. This surface can then be wiped with a pliable brush, such as a 65 ppi foam to improve surface uniformity.

The proper spray viscosity is dependent on the ceramic composition. For instance, in a zirconia system, 65 partially stabilized with magnesia, a viscosity range of 1000 to 6000 centipoise may be used with 4000

centipoise being preferred. In a mullite system, a spray viscosity ranging from 250 to 4000 centipoise may be used with 1500 centipoise being preferred.

A slip coated system applied by a doctor blade principle is applicable to all pore sizes. A typical formulation for a 2000 gram batch of alumina coating slurry is as follows:

5	Alumina	1,960 grams	5
	Silica	100 grams	
	Organic binder	200 grams	
	Surfactant	5 milliliters	
10	H ₂ O	750 milliliters	10

Again in this process the slip coating viscosity is dependent on composition. A slip coating viscosity for the above example would range from 20,000 centipoise to 30,000 centipoise with a preferred viscosity being 15 25,000 centipoise. The mullite composition would have a viscosity of 22,000 centipoise. The zirconia, partially stabilized with MgO system has a slip coating viscosity range of 15,000 to 40,000 centipoise with a preferred viscosity being 25,000 to 30,000 centipoise.

The slip coating is applied by having the parts moving on a conveyor with controllable speed and passing under a stiff rubber blade. The distance between the blade and the surface of the part can be accurately 20 controlled. The slurry is dispensed as evenly as possible in front of the blade which coats the surface of the reticulated ceramic as it moves by. The parts are placed in a dryer at 60°C with moving air with drying time being dependent on part size.

After drying the coated ceramics are fired or burned at a temperature and for a time appropriate to their compositions. These times and temperatures are well known by those skilled in the ceramic arts.

25 Pore size, web and coating thickness of coated ceramics according to this invention can be measured, for example, using a binocular zoom microscope with calibrated filar eyepiece. In the following table, typical measurements for coated ceramics according to this invention are set forth.

30		10 ppi Slip Coated	20 ppi Slip Coated	30 ppi Slip Coated	65 ppi Spray Coated	65 ppi Slip Coated	100 ppi Spray Coated	100 ppi Slip Coated	30
	Coating thickness (mm)	2.36	2.31	1.40	0.40	0.625	0.53	0.45	
35	Pore size (mm)	1.3	0.76	0.6	0.28	0.35	0.23	0.25	35
	Web thickness (mm)	0.66	0.40	0.36	0.07	0.07	0.07	0.05	
	Coating/Web thickness ratio	3.6	5.6	3.9	5.3	8.3	7	9	
40									40

The 90 and 98% alumina, mullite and stabilized zirconia coated reticulated ceramic shapes described herein are useful for molten metal filtration, corrosion resistant catalytic supports, light weight insulation, 45 low mass kiln furniture and specialty refractories. The lithium aluminosilicate coated reticulated ceramic shapes described herein are useful for catalytic supports and pollutant particle traps for gasoline, diesel and woodburning stoves.

Having thus described the invention with the detail and particularity required by the Patent Laws, what is desired to be protected by Letters Patent is set forth in the following claims.

50 CLAIMS

1. A ceramic structure comprising:
a) a reticulated ceramic portion having a plurality of interconnecting webs; and
55 b) a ceramic sheet or coating portion sintered to the webs along a surface defined by one side of said sheet or coating portion, the ratio of the average thickness of said sheet or coating portion to the average thickness of the interconnecting webs being less than ten.
2. A ceramic structure comprising:
a) a reticulated ceramic portion having a plurality of interconnecting webs; and
60 b) a ceramic sheet portion sintered to the webs along a surface defined by one side of said sheet portion, said sheet portion having a thickness less than the average thickness of the interconnecting webs.
3. A ceramic structure according to Claim 2 wherein the average thickness of said interconnecting webs is less than about one millimeter.
4. A ceramic structure according to Claim 3 wherein the thickness of said sheet portion is less than about 65 0.5 millimeter.

5. A method of manufacturing a ceramic structure comprising the steps of:
 a) preparing a reticulated ceramic;
 b) preparing a leather-hard ceramic sheet;
 c) applying a ceramic slurry to said reticulated ceramic without filling the pores at the surface and laying
 5 said sheet against said reticulated ceramic where said slurry has been applied; ad
 d) firing the composite structure.
6. A method of manufacturing a ceramic structure comprising the steps of:
 a) preparing a reticulated ceramic defined by a plurality of interconnecting webs with a continuous pore
 phase therebetween;
 10 b) preparing a leather-hard ceramic sheet having a thickness less than the average thickness of said
 interconnecting webs;
 c) applying a ceramic slurry to the exposed webs of said reticulated ceramic at a face thereof without filling
 the pores at the surface and laying said leather-hard ceramic sheet against the exposed webs to which the
 slurry has been applied; and
 15 d) drying and firing the composite structure to produce a sintered ceramic structure.
7. The methods according to Claims 5 or 6 wherein said slurry is prepared from a finely divided ceramic
 material and said leather-hard sheet is prepared to include a major amount of the same ceramic material.
8. A ceramic article defining a filter for molten metal comprising a reticulated ceramic portion having a
 plurality of interconnecting webs and a ceramic sheet portion wrapping a surface of said reticulated ceramic
 20 portion substantially parallel to the direction of flow through the filter and said sheet portion being sintered
 to said webs.
9. A ceramic article defining a heat exchanger comprising two reticulated ceramic portions having a
 plurality of interconnecting webs and a ceramic sheet portion therebetween and sintered thereto and means
 to direct flow of hot fluids through the reticulated ceramic on one side of said sheet portion and means to
 25 direct flow of cooling fluid through the reticulated ceramic on the other side of said sheet portion.
10. A ceramic article defining kiln comprising a reticulated ceramic base portion having a plurality of
 interconnecting webs and a surface shaped to support the ware to be carried by the furniture and a ceramic
 sheet portion conforming to the shape of said surface and sintered to said webs.
11. A ceramic article according to Claims 8,9, or 10 wherein said sheet portion has a thickness less than
 30 the average thickness of said interconnecting webs.
12. A ceramic article according to Claim 11 wherein the average thickness of said interconnecting webs is
 less than about one millimeter.
13. A ceramic article according to Claim 12 wherein said sheet portion has a thickness less than about 0.5
 millimeter.
- 35 14. A ceramic structure comprising at least two reticulated ceramic portions defined by a plurality of
 interconnecting webs, one reticulated portion having a finer pore size than the other and a ceramic sheet
 portion sintered to the webs of the finer reticulated portion along a surface defined by one side of said sheet
 portion, said sheet portion having a thickness less than the average thickness of the interconnecting webs of
 the finer reticulated portion.
- 40 15. A ceramic article defining kiln furniture comprising a reticulated ceramic base portion comprised of
 a plurality of interconnecting webs and having a surface shaped to support the ware to be carried by the
 furniture, said reticulated portion being comprised of two layers, one of finer pore size than the other, the
 finer layer being adjacent said shaped surface and a ceramic sheet portion conforming to the said shaped
 surface and sintered thereto.
- 45 16. A ceramic furnace liner comprising a rigid ceramic structure being a reticulated ceramic portion
 defined by a plurality of interconnecting webs and a ceramic sheet portion sintered to said webs along a
 surface defined by one side of said sheet, said sheet having a thickness less than the average thickness of the
 interconnecting webs and a slightly compressible ceramic fiber refractory material bonded to said
 reticulated ceramic portion with a refractory cement.
- 50 17. A ceramic furnace liner comprising:
 a rigid ceramic structure having at least one reticulated ceramic portion defined by a plurality of
 interconnecting webs and at least two substantially parallel ceramic sheet portions sintered to said webs
 along surfaces defined by said sheet portions, said sheet portions having a thickness less than the average
 thickness of said interconnecting webs and said sheet portions being oriented substantially perpendicular to
 55 the direction of heat flow.
18. A ceramic structure comprising:
 a) a reticulated ceramic portion defined by a plurality of interconnecting webs having a pore distribution of
 between 5 and 125 pores per linear inch and
 b) a ceramic coating portion sintered to the webs along a surface defined by one face of said coating
 60 portion, said coating portion having a thickness less than 3 millimeters, and the ratio of average thickness of
 said web forming the reticulated ceramic to the thickness of said coating portion being between 1 and 10.
 19. A method of manufacturing a ceramic structure comprising the steps of:
 a) preparing a reticulated ceramic having a plurality of interconnecting webs having a pore distribution
 between 125 and 65 pores per linear inch,
 65 b) spraying a ceramic slurry upon at least one surface of the reticulated ceramic to form a coating less than

- about 0.5 millimeter thick, and
c) firing the composite structure.
20. The method according to Claim 19 wherein the ceramic slurry has a viscosity of between 250 and 6000 centipoise and the coating has a thickness between about 0.25 and 0.5 millimeter.
- 5 21. A method of manufacturing a ceramic stucture comprising the steps of: 5
a) preparing a reticulated ceramic having a plurality of interconnecting webs having a pore distribution between about 125 and about 5 pores per linear inch,
b) trowling a ceramic slip upon at least one surface of said reticulated ceramic to form a coating less than 3 millimeters thick, and
10 c) firing the composite structure. 10
22. The method according to Claim 21 wherein said ceramic slip has a viscosity of between 15,000 and 40,000 centipoise and said coating has a thickness between about 0.5 and 3 millimeters.
23. A ceramic article or structure comprising at least one reticulated ceramic portion having a plurality of interconnecting webs.
- 15 24. A method of manufacturing a ceramic structure comprising forming at least one reticulated ceramic portion. 15
25. A ceramic article or structure substantially as hereinbefore described with reference to and as shown in the accompanying drawings.
26. A method of manufacturing a ceramic structure substantially as hereinbefore described with 20 reference to the accompanying drawings.
27. Any novel integer or step, or combination of integers or steps, hereinbefore described and/or shown in the accompanying drawings, irrespective of whether the present claim is within the scope of, or relates to the same or a different invention from that of, the preceding claims.
- 25 Amendments to the claims have been filed, and have the following effect:- 25
(a) Claims 22,23,24,27 above have been deleted or textually amended.
(b) New or textually amended claims have been filed as follows:-
22. The method according to claim 21 wherein said ceramic slip has a viscosity of between 15,000 and 40,000 centipoise and said coating has a thickness between 0.5 and 3 millimeters.
30 (c) Claims 25 & 26 above have been re-numbered as 23 & 24 and their appendancies corrected. 30

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